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(58) Field of search  
C1H

(54) Foamed cement compositions for stowing cavities

(57) Compositions suitable for the production of foamed cements comprise an hydraulic cement clinker (for example a mixture of ordinary Portland cement with a high alumina cement or a  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ -rich clinker), calcium sulfate, an air-entraining or foaming agent (especially an anionic sulfated or sulfonated organic surfactant) and a stabilising agent (especially a cellulose ether). Instead of the hydraulic cement clinker, a potentially hydraulic mineral clinker may be used in the presence of an activator, for example calcium oxide and/or hydroxide. The composition may also comprise an extender (for example blast furnace slag), a clay (for example bentonite) and setting accelerators, for example inorganic salts (for example alkali metal carbonates). The compositions may be made up with water and then foamed by the introduction of a gas, for example air, the resultant foamed cement being especially useful for filling cavities in underground mines.

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## SPECIFICATION

## Foamed cement compositions for stowing cavities

5 *Field of the invention*

This invention relates to compositions suitable for the production of quick-setting, low density, foamed cements that are flowable materials and that can be pumped into cavities. Such foamed cements are especially useful for filling cavities in underground mines.

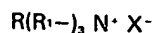
10 *Background to the invention*

The natural presence of fissures, cavities or porous surfaces (herein collectively referred to as cavities) or their formation during the course of mining or drilling due to weaknesses in the strata can often adversely affect the economic recovery of minerals, oil and gas.

In underground mining operations cavities may present a safety hazard and/or restrict the flow of materials along the access tunnels. In drilling operations, where a well cement pumped as a slurry is used to seal the annular space between the walls and the steel casing through which the material being extracted is carried, a significant quantity of cement may be lost to the strata. To prevent such losses materials such as expanded perlite, vermiculite, crushed coal or gilsonite (known collectively as loss circulation controllers) are often incorporated in the well cement slurry to help seal the surface and/or fill the cavity. However, delivery of these materials to the well site, particularly an off-shore well, may prove costly, while their incorporation in a cement slurry often results in the slurry being more difficult to pump.

An alternative way to fill a cavity encountered during drilling is to use a foamed cement, which offers the advantages that less material is required to fill a given void or cavity; the weight of the filling medium is not excessive and is less likely to lead to the breakdown of other weak formations; the mixture is easily pumped; and if necessary the filling medium can be readily redrilled. Traditionally, in the oil or gas drilling industry, foamed cements are produced by incorporating additives in the well cement that is being used to fill the annular space. The resultant foamed cementitious mixture is then pumped down the well in a similar way to the normal well cementing operation. One way of producing a foamed cement is to add to the cementitious mix an active metal, such as aluminium or magnesium, which reacts with the cement slurry to generate hydrogen gas *in situ*. Such a technique, together with the use of chemical inhibitors to control the release of gas, to produce a foamed well cement for sealing zones penetrated while drilling is described in British Patent Specification 2,104,055A.

Another way of producing a foamed cement is to add a "foaming agent", typically a surfactant, to the well cement slurry such that any air or gases introduced into the slurry are encapsulated and trapped in it. In British Patent Specification 2,119,358A there is described the use of a foaming agent represented by the formula



wherein X is chloride, bromide, iodide or hydroxyl, R is an aliphatic hydrocarbyl radical having from 8 to 16 carbon atoms and R' is, independently each occurrence, an alkyl radical of one to three carbon atoms or hydroxyethyl, and the sum of the carbon atoms in R and all R' is not greater than 20.

Both methods as described above for producing a foamed cement are particularly suited for use with the Basic Class G and Class H well cements as defined in American Petroleum Institute Specification 10 1982. These cements can be used to prepare a neat cement slurry on the surface for then pumping down to depths up to 8000 feet (2438 m) or they can be mixed with retarders and other additives such that they can be pumped to greater depths.

In mining operations, and in coal mining in particular, traditional practice has been manually to seal and/or fill cavities encountered underground with timber chocks. However, this is both expensive and time-consuming. Such methods also rarely result in a perfect seal against the possible seepage of gases.

In coal mining operations the use of foamed cement to fill cavities would be attractive in that the quantity of materials taken below ground would be minimised and the resulting filling medium would be relatively impermeable. However, whereas in the drilling industry compositions with relatively long setting times are required so that the mixture can be mixed on the surface and then pumped to considerable depths, the mixing operation in coal mining is likely to take place underground such that the pumping distance is relatively short: thus, in order to minimise stoppages and effect a quick repair the foamed cement should preferably have a rapid setting time.

Such short setting times cannot be achieved with conventional or normal well cements unless they are mixed with accelerators. Unfortunately, when conventional foaming agents are also added to such mixtures the results are often erratic and variable, especially in coal mines where contamination with coal or waste material can retard the setting of normal cements. A further requirement of foamed cements to be used in underground mines is that they should not present a safety hazard: for this reason the use of metals to generate hydrogen gas *in situ* as described in British Patent Specification 2,104,055A is not acceptable. Synthetic foams, on the other hand, are more expensive and in some instances, such as with

urea formaldehyde foam, can also present a safety hazard as the emission of formaldehyde fumes is unpleasant and in the event of combustion hydrogen cyanide gas could be evolved.

Over the last decade a number of quick-setting cements have been developed for binding supportive packs adjacent to roadways leading to longwall coal faces and their use for this purpose is now well

5 known.

British Patent Specifications 1,387,075 and 1,497,670 disclose a quick setting, early strength cement suitable for use in the process described in British Patent Specification 1,362,954. This cement comprises 7-90% usually 10-70% and preferably 15-30%, by weight of the hydraulic constituents, of the calcium aluminate phase  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ , together with the other hydraulic phases commonly found in cements the bulk of which are calcium silicates. The cement may also comprise calcium sulfate and small additions of a retarder, such as citric acid, and of an accelerator, such as potassium sulfate.

Another method of constructing suitable packs adjacent to roadways leading to longwall coal faces is described in British Patent Specification 2,058,037A, in which an aqueous slurry containing a cement, or cement mixture, is concurrently injected into the pack with a second aqueous slurry containing a clay and an inorganic salt which accelerates the setting and hardening of the cement. Suitable cement mixtures are described which comprise ordinary Portland cement, a calcium aluminate, calcium sulfate and a carboxylic or hydroxycarboxylic acid or a salt of such an acid. The ratio of the weight of calcium aluminate to the weight of calcium sulfate is typically from 3:1 to 1:3 and the weight of the mixture of these components is generally from 10 to 75% of the weight of the Portland cement. The preferred calcium aluminate is  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , which is readily available as High Alumina cement. A typical cement slurry is said to comprise a cement mixture and water mixed in a ratio of 0.5:1 to 2:1 by weight where the cement mixture contains 66.65% ordinary Portland cement, 18.4% High Alumina cement, 14.7% anhydrous calcium sulphate and 0.25% citric acid, whereas a typical clay slurry comprises bentonite and sodium carbonate such that the bentonite is present in an amount of between 0.25% and 10% by weight of the water and the sodium carbonate is present in an amount equivalent to between 1% and 10% by weight of the cement in the cement slurry. When concurrently injected into a cavity the final mix typically consists of the cement mixture, bentonite and water substantially in the proportions of 14%, 1% and 85% by volume.

A method of constructing packs similar to those described in British Patent Specification 2,058,037A is disclosed in British Patent Specification 2,123,808A, in which a first slurry comprising High Alumina Cement is mixed with a second slurry comprising beta-anhydrite and calcium oxide and/or calcium hydroxide, the second slurry usually also containing a clay, typically bentonite, and an accelerator of High Alumina cement, such as lithium carbonate. The resultant cement composition will usually contain High Alumina cement and beta-anhydrite in a ratio of from 3:7 to 4:1 by weight, whereas the calcium oxide and/or calcium hydroxide added will preferably range from 2 to 8.5%, typically 3.5 to 5%, by weight. Small additions of gypsum or an alkali metal sulfate such as potassium sulphate can also be made. The composition of the bentonite mix will be such that when mixed with the cementitious mix the quantity of bentonite will usually be between 10 and 25% by weight of the beta-anhydrite, whereas the quantity of lithium carbonate will usually be up to 1%, typically between 0.05 and 0.2%, by weight of the High Alumina cement.

Such quick-setting cementitious compositions as disclosed in British Patent Specifications 1,387,025; 1,497,670; 2,058,037A and 2,123,808A would be ideally suited for use with a foaming agent to produce a lightweight foamed cement that could be used to fill cavities in underground mining. Indeed, the use of compositions as disclosed in British Patent Specification 2,058,037A together with a foaming agent for such purposes is already being practised in some collieries in the United Kingdom.

Accordingly, an object of the present invention is to provide a means of foaming cementitious compositions in order that they can be used to form a durable light weight filling medium which can be used for filling cavities in underground mining. A further object of the present invention is to provide a means of foaming cementitious compositions which is comparatively cheap, which produces a stable foam even with a quick-setting cement, which can produce a foam with a good structure (especially with discrete, uniformly sized gas bubbles) and which permits the production of a filling medium that has good properties even in a wet environment.

#### *Summary of the invention*

The present invention provides a composition suitable for the production of a foamed cement, said composition comprising (a) a ground, mineral clinker selected from (i) hydraulic cement clinkers, (ii) potentially hydraulic mineral clinkers and (iii) mixtures thereof, (b) calcium sulfate, (c) an air-entraining agent and (d) a stabilising agent.

Preferably, the composition of this invention comprises (a) from 20 to 99% of the mineral clinker, in particular 40 to 99% (especially when a mixture (iii) is employed), and typically 65 to 99% of a cement clinker (i) or 40-60% of a mineral clinker (ii), (b) from 1 to 76%, typically from 1 to 20%, of calcium sulfate, (c) from 0.02 to 1%, typically from 0.05 to 0.1%, of air-entraining agent and (d) from 0.05 to 3%, typically from 0.1 to 2%, of stabilising agent, the stated amounts of components (a)-(d) being relative to the total composition on a dry weight basis.

The composition may also contain one or more additional components, for example extenders, clays

and setting accelerators. If required, a setting retarder, e.g. citric acid, may be included, typically in an amount of 0.1 to 3% by weight.

In use, the compositions of the present invention will be made up with water. The resultant aqueous compositions are quick-setting, flowable and capable of being formed into foams that have a stable  
5 structure of discrete, uniformly sized bubbles and that are suitable for use as low-density filling media.

Accordingly, the present invention also provides a method of forming a foamed cement, characterised in that a composition according to this invention is mixed with water and a gas is introduced into the aqueous mixture to form a foam. Thus, a cavity may be filled by introducing such a foam into the cavity (either by injecting the foam into the cavity or by forming the foam *in situ*) and allowing the foamed  
10 composition to set.

#### *Description of preferred embodiments*

Component (a) of the cementitious composition of this invention may be High Alumina cement clinker, preferably in the presence of an inorganic salt such as lithium carbonate (which salt will act as a setting  
15 accelerator) as disclosed in British Patent Specification 2,123,808A (the teaching of which is incorporated herein by reference). In such embodiments, the composition may include calcium oxide and/or calcium hydroxide, preferably in an amount to ensure that lime and alumina are present in appropriate molecular proportions to form ettringite during hydration.

Component (a) may alternatively be a mixture of ordinary Portland cement clinker and High Alumina cement clinker, preferably in the presence of an inorganic salt such as sodium carbonate (which salt will  
20 act as a setting accelerator), as disclosed in British Patent Specification 2,058,037A (the teaching of which is incorporated herein by reference).

In preferred embodiments, however, component (a) will comprise a ground clinker that is rich in  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  (usually abbreviated to  $\text{C}_{12}\text{A}_7$ ). Such a clinker is described in detail in British Patent Specification 1,387,075 (the teaching of which is incorporated herein by reference) and may be produced by  
25 fusing or sintering, generally at a temperature above  $1250^\circ\text{C}$ , a mixture of siliceous material (e.g. a kaolinitic clay such as china clay, ball clay or fire clay), calcareous material (e.g. chalk or limestone) and aluminous material (e.g. bauxite) proportioned to yield a product rich in  $\text{C}_{12}\text{A}_7$  (i.e. having a  $\text{C}_{12}\text{A}_7$  content of 7-90%, usually 10-70% and typically from 15-50%, by weight of the clinker) and poor in  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  (ab-  
30 breviated to CA) or  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  (abbreviated to  $\text{C}_3\text{A}$ ). When the mixture is fired under conditions to provide an uncombined lime content of less than 5%, a  $\text{C}_{12}\text{A}_7$ -rich clinker is obtained, the major calcium silicate phase of which is dicalcium silicate ( $2\text{CaO} \cdot \text{SiO}_2$ , abbreviated to  $\text{C}_2\text{S}$ ) with a calcium aluminoferrite ( $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ , abbreviated to  $\text{C}_4\text{AF}$ ), magnesia, alkali metal sulfate and alkali metal calcium double sulfate also being present in minor amounts.

As described in British Patent Specification 1,497,670 (the teaching of which is also incorporated herein  
35 by reference), the  $\text{C}_{12}\text{A}_7$ -rich clinker may be underlimed, an underlimed clinker being one in which the lime limitation factor (LLF) is less than unity, where

$$\text{LLF} = \frac{\text{CaO}}{1.87 \text{ SiO}_2 + 0.94 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3}$$

the chemical symbols representing the amounts by weight of the represented substances that are present, the underlimed condition being at least counterbalanced in the cement by the presence of a sub-  
45 stance effective to increase the basicity of the cement.

The said substance effective to increase the basicity of the cement may be a metal oxide, e.g.  $\text{MgO}$  or  $\text{FeO}$ , present in the  $\text{C}_{12}\text{A}_7$ -rich clinker in solid solution in substitution for  $\text{CaO}$  in the lattices of major phases. Alternatively, the said substance effective to increase the basicity may be a source of calcium ions, e.g. calcium chloride, calcined lime or calcium hydroxide, added to the cement.

The hydraulic clinker constituting component (a) of the present composition may contain a mixture of  
50 the  $\text{C}_{12}\text{A}_7$ -rich clinker with, for example, Portland cement especially ordinary Portland cement. Such a cement mixture may be formed conveniently by intergrinding the  $\text{C}_{12}\text{A}_7$ -rich clinker and ordinary Portland cement clinker, usually together with a source of sulfate, a small quantity of a retarder known as such, e.g. a sugar, a lignosulfonate or, especially, citric acid, and a small quantity of inorganic salt.

Suitable inorganic salts include known accelerators of cement such as halides, nitrites, borates, hydroxides, bicarbonates, carbonates and sulfates (other than, of course, the calcium sulfate present  
55 as component (b)), including the alkali metal (e.g. lithium, sodium or potassium), alkaline earth metal (e.g. calcium or magnesium) and aluminium salts. Preferred salts are alkali metal carbonates, alkali metal sulfates and calcium chloride. Potassium carbonate and, especially, sodium carbonate are particularly  
60 preferred.

When the  $\text{C}_{12}\text{A}_7$ -rich clinker is underlimed, as described above, the substance effective to increase the basicity of the cement may be a source of calcium ions provided in the form of uncombined lime in the Portland cement clinker.

Instead of hydraulic cement clinkers, for example those described above, component (a) may be se-  
65 lected from potentially hydraulic mineral clinkers, that is to say clinkers that require the presence of one

or more activating agents before they will exhibit a significant hydraulic activity. Preferred clinkers of this type are based upon the mineral phase  $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$  (which may be abbreviated to  $\text{C}_4\text{A}_3\text{S}$ ), which is commonly known as Klein's compound, a particularly preferred mineral clinker being one that contains at least 25% by weight of  $\text{C}_4\text{A}_3\text{S}$ , not more than 1% by weight of free lime, less than 5% by weight of  $\text{CA}_2$  and not more than 10% by weight of  $\text{C}_{12}\text{A}_7$ . Although  $\text{C}_4\text{A}_3\text{S}$  reacts hydraulically only very slowly with plain water, the ground clinker may be set by mixing it with water in the presence of a source of alkali metal or alkaline earth metal under alkaline conditions. Such conditions in use are preferably obtained using calcium oxide and/or calcium hydroxide, it being convenient to incorporate such an activator or activators in the initial dry composition.

It is preferred that the mineral clinker (activated, if necessary) should be such that when the composition is made up as a slurry containing water in an amount of 80 to 350% by weight of component (a) the initial setting time of that slurry is preferably 30 minutes or less, typically 15 minutes or less.

The amount of calcium sulfate present as component (b) of the present composition is calculated as the anhydrous material. The preferred form of calcium sulfate is the dihydrate form,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , which can be either natural gypsum or a synthetic gypsum such as the by-product from an acid-producing plant, although if the latter is used account must be taken of the effect that any trace impurities in the synthetic gypsum, such as fluorine or phosphorus, may have on the setting and hydration of the cement.

Of course, other forms of calcium sulfate may be employed; for example, it may be preferred to use beta-anhydrite when High Alumina cement clinker is employed as component (a) in the presence of calcium oxide and/or calcium hydroxide.

As indicated above, sulfate may be used in the preparation of the hydraulic cement clinker. Any calcium sulfate introduced in this manner is regarded as part of component (b), rather than component (a), for the purpose of determining the amounts of the components.

The air-entraining agent (c) can be, for example, an animal or vegetable fat or oil, a natural wood resin or an alkali metal salt thereof, a sulfated or sulfonated organic compound (usually in the form of an alkali metal or ammonium salt), or an amphoteric surfactant such as an alkyl imidazoline derivative. Such of these materials that are conventionally known as foaming agents are preferred. Particularly preferred are anionic surfactants, for example the sulfated or sulfonated organic compounds, especially alcohol sulfates, ether sulfates and alkyl benzene sulfonates.

The stabilising agent (d) can be, for example, a gelatine, a starch (which term includes starch derivatives) or a cellulose ether. The cellulose ethers are preferred, amongst which may be mentioned hydroxyethyl cellulose, methyl cellulose, hydroxypropyl methyl cellulose and (sodium) carboxymethyl cellulose. The cellulose ethers will usually have a Brookfield viscosity of 1,000 to 10,000 mPa.s, typically 2,500 to 7,500 mPa.s (as measured on a 2% aqueous solution at 25°C).

It is particularly preferred that the composition comprise an anionic surfactant selected from sulfated or sulfonated organic compounds as component (c) in combination with a cellulose ether as component (d), the most favoured combination at present being an alcohol sulfate or ethoxy sulfate foaming agent with methyl hydroxyethyl cellulose. Such combinations have been found to provide remarkably uniform and stable gas bubbles in the foamed structure, even when a quick-setting cement is employed. This is surprising, since the use of a quick-setting cement will give rise to localised regions of high temperature during the hydration reaction, which would have been expected to cause disruption of the bubble structure.

The composition of the present invention may optionally contain (e) an extender, for example a granulated blast furnace slag or another latently hydraulic material such as pulverised fuel ash, a natural pozzolana or a synthetically produced pozzolanic material. Such an extender, if used, will usually be present in an amount of up to 30%, relative to the total composition on a dry weight basis.

The present composition may also contain, if required, (f) a clay, for example a hectorite, bentonite, smectite or kaolinite clay, amongst which bentonite (e.g. the calcium form or, especially, sodium-activated bentonite) is preferred. If used, the clay will usually be present in an amount of from 0.5 to 10%, preferably from 4 to 6%, relative to the total composition on a dry weight basis.

As indicated above, the composition of the present invention may also contain (g) an inorganic salt (other than the calcium sulfate component), especially as a setting accelerator for the cement component. If used, the inorganic salt (preferably an alkali metal salt, especially a carbonate) will usually be present in an amount of from 2 to 10%, preferably from 4 to 6%, relative to the total composition on a dry weight basis, as disclosed in British Patent Application No.8513786 (the teaching of which is incorporated by reference). Of course when the cement clinker component is as described in British Patent Specification No.1,387,075, No.1,497,670, No.2,058,037A or No.2,123,808A, then it may be advantageous to adopt the recommendations in the relevant specification with regard to the nature and the amount of the inorganic salt.

It will be understood, of course, that each of the components (a) to (g) may be constituted by a mixture of suitable compounds, if desired.

As also indicated above, the composition may comprise (h) calcium oxide, calcium hydroxide or a mixture thereof. It is preferred that these bases, if used, should be present in a total amount not exceeding 20%, relative to the total composition on a dry weight basis.

In use, the composition of the present invention will be made up with water and with a gas, usually air,

preferably by mixing and pumping in a foam-generating machine which will allow a controlled amount of the gas to be encapsulated in the composition. A typical suitable foam-generating machine consists of a two-speed mono-pump placing machine in which the dry components are fed into a mixing trough with water. The resultant slurry is then pumped to the point of application along a hose into which is

5 sucked the surrounding gas, usually air. By varying the length and diameter of the discharge hose the amount of air encapsulated in the foam and thus its resultant density and strength can be adjusted to give the desired results.

The water content of the foamed aqueous composition is preferably from 80 to 350% by weight of the clinker component (a). The amount of gas encapsulated in such foamed aqueous compositions may typically be in the range of from 86 to 95% when expressed on a volume basis; as a result, the dry density of the foamed cement when set will typically be in the range of from 150 to 400 kg per cubic metre.

Although the individual components of the above mixture can be introduced separately into a mixing and foaming machine in the desired proportions, it has been found beneficial to produce an initial dry mixture by intergrinding at least some, and preferably all, of the components. By intergrinding the air-entraining (foaming) and stabilising agents (c) and (d) with at least the components (a) and (b) it has been found that a better distribution of these agents is achieved with the result that the same degree of foaming can be obtained with an overall lower level of additives (c) and (d) than would be the case if they were added separately at the mixing stage. As a consequence, use of costly additives is minimised and relatively cheap, quick-setting foamed cavity-filling media can be produced, such media exhibiting a

20 good stability even under wet conditions.

It may be regarded as surprising that such good results can be obtained when the components are interground, since it would have been expected that the high temperatures generated during the intergrinding process would cause degradation of the stabilising agent.

The quick-setting foamed cements of the present invention are ideally suited in coal mines for filling cavities in the coal face area, above roadways, at the heads of roadways, where falls have occurred and for sealing off side roadways in the return method of retreat mining.

It is not, however, envisaged that this invention should be restricted just to the above-described coal-mining applications. The combination of a foaming agent and a stabilising agent as described herein may be added to any hydraulic cement where it is desirable to produce a light-weight structure or to limit the quantity of materials employed. Nor is it necessary that the cement should only be foamed by itself to form a filling medium, for other solid constituents, such as fibres, fillers and light-weight aggregates, can also be incorporated in the mix, if required. The present foamed cement, it is envisaged, can also be used to provide insulation against heat and sound or to protect fragile objects:

The following examples serve to illustrate the invention. Percentages and parts are by weight, unless otherwise stated.

#### Example 1

A composition comprising 70.66% ordinary Portland cement clinker, 4.14% gypsum, 25%  $C_{12}A_7$ -rich clinker, 0.1% of the foaming agent Fenopon CD-128 (an ethoxy sulfate, ammonium salt, from G.A.F. (Great Britain) Ltd.) and 0.1% of the cellulose ether thickening agent Tylose P60002 (an hydroxypropyl methyl cellulose; Brookfield viscosity 6000 mPa.s measured on a 2% aqueous solution at 25°C) was inter-

40 ground at a temperature of 70°C in a batch ball mill to a surface area of 400 m<sup>2</sup>/kg.

The resultant cement was mixed at time intervals of 1, 2 and 5 minutes with 80, 90 and 100% by weight of water on the dry mix in a Hobart mixer with whisk at the speed setting 2, made into 100 mm

45 cubes and cured at 20°C and 100% relative humidity.

The specimens were tested for comparative strength at 7 days and after breaking were measured for dry density.

The results are shown in the table below.

	Mixing Water (%)	Mixing Time (Mins)	Dry Density (kg/m <sup>3</sup> )	Comparative Strength (p.s.i.)	
50	100	2	153	6	
55	90	1	175	10	
	80	5	233	16	
	80	1	380	25	

#### Example 2

60 A composition comprising 55.84% ordinary Portland cement clinker, 3.96% gypsum, 20%  $C_{12}A_7$ -rich clinker, 20% pulverised fly ash, 0.1% Fenopon CD-128 and 0.1% Tylose P60002 was prepared and tested in the same way as that in Example 1 to give the following results:

	Mixing Water (%)	Mixing Time (Mins)	Dry Density (kg/m <sup>3</sup> )	Comparative Strength (p.s.i.)	
5	100	2	175	4	5
	100	1	182	7	
	90	1	281	18	
	80	1	306	23	

10 *Example 3*

A composition comprising 29.09% C<sub>2</sub>A<sub>7</sub>-rich clinker, 43.71% ordinary Portland cement clinker, 2.66% gypsum, 0.30% citric acid, 13.82% synthetic anhydrite, 6.06% sodium carbonate, 4.16% bentonite, 0.1% Fenopon CD-128 and 0.1% Tylose P60002 was prepared and tested as in Examples 1 and 2 except that only specimens containing 90% and 100% by weight water on the dry mix were prepared and tested at

15 mixing times of 2 and 1 minute respectively.

The results are shown in the table below.

	Mixing Water (%)	Mixing Time (Mins)	Dry Density (kg/m <sup>3</sup> )	Comparative Strength (p.s.i.)	
20	90	2	170	26	20
	100	1	210	33	

25 *Example 4*

A mineral clinker was prepared from a raw feed mix comprising bauxite, limestone and anhydrite, which raw mix was slurried in water and fed to a coal-fired rotary kiln in which it was sintered at 1450°C. A small amount of coal ash was incorporated into the material during sintering.

The resultant clinker had the following chemical analysis: SiO<sub>2</sub> 5.4%, Al<sub>2</sub>O<sub>3</sub> 45.5%, Fe<sub>2</sub>O<sub>3</sub> 1.3%, CaO 38.2%, MgO 0.4%, Mn<sub>2</sub>O<sub>3</sub> less than 0.01%, P<sub>2</sub>O<sub>5</sub> 0.13%, TiO<sub>2</sub> 2.1%, total S (expressed as SO<sub>3</sub>) 6.3%, K<sub>2</sub>O 0.23% and loss on ignition 0.1%.

The composition of the mineral clinker was calculated to be: C<sub>2</sub>A<sub>3</sub>S 48%, CA 15.7%, C<sub>2</sub>A, 2.5%, C<sub>2</sub>AS 24.6%, C<sub>2</sub>AF 4.0%, CT 3.9%, with CA<sub>2</sub> and CaSO<sub>4</sub> being substantially absent.

The mineral clinker was mixed with 0.25% citric acid and 0.3% guar gum and was then ground to a specific surface area of 450 m<sup>2</sup>/kg, the particle size distribution being such that 10% residue remained on a sieve of 350 micron mesh size. 50 parts of the resultant ground clinker were mixed with 0.05 part Fenopon CD-128, 1.5 parts Tylose P60002, 0.1 part citric acid and 50 parts of a mixture consisting of 76.1% synthetic anhydrite, 18.0 parts calcium hydroxide (Hydralime, from Blue Circle Industries PLC), 5.0% bentonite clay, 0.5% sodium carbonate and 0.4% lithium carbonate. The resultant cement was mixed at time intervals of 0.5, 1 and 3 minutes with, in each case, 150% by weight of water on the dry mix, the mixing and the subsequent testing being carried out as described in Example 1. The results are shown in the following table.

	Mixing Water (%)	Mixing Time (Mins)	Dry Density (kg/m <sup>3</sup> )	Comparative Strength (p.s.i.)	
45	150	0.5	333	170	45
	150	1	253	65	
50	150	3	109	15	50

*Comparative Example A*

A cement composition was prepared by mixing 50 parts of the ground mineral clinker described in Example 4 with 50 parts of a mixture of synthetic anhydrite, Hydralime bentonite, sodium carbonate and lithium carbonate, also as described in Example 4, in the presence of 0.2 part of Tylose P 60002 and 0.1 part of Arquad 18-50% (a commercially available surfactant based on an alkyl quaternary ammonium chloride). The resultant cement was mixed with 200% by weight of water on the dry mix in the manner described in Example 1. However, the foam produced was clearly unstable and the cement composition was therefore deemed to be unsuitable for the industrial production of foamed cement.

60 The words "Fenopon", "Tylose", "Hydralime" and "Arquad" used hereinabove are understood to be trademarks.

It will of course be understood that the present invention has been described above purely by way of example, and modifications of detail can be made within the scope of the invention.

## CLAIMS

1. A composition suitable for the production of a foamed cement, said composition comprising (a) a ground mineral clinker selected from (i) hydraulic cement clinkers, (ii) potentially hydraulic mineral clinkers and (iii) mixtures thereof, (b) calcium sulfate, (c) an air-entraining agent and (d) a stabilising agent. 5
2. A composition according to claim 1, characterised in that it contains (a) from 20 to 99% of the mineral clinker, (b) from 1 to 76% of calcium sulfate, (c) from 0.02 to 1% of air-entraining agent and (d) from 0.05 to 3% by weight of stabilising agent, the stated amounts being relative to the total composition on a dry weight basis.
- 10 3. A composition according to claim 1 or 2, characterised in that the mineral clinker (a) is such that when the composition is made up as a slurry containing water in an amount of 80 to 350% by weight of component (a) the initial setting time of that slurry is 15 minutes or less. 10
4. A composition according to claim 1, 2 or 3, characterised in that the mineral clinker is selected from High Alumina cement, in the presence of sufficient calcium oxide and/or calcium hydroxide to ensure that lime and alumina are present in the appropriate molecular proportions to form ettringite during hydration; mixtures of ordinary Portland cement clinker and High Alumina cement clinker; clinkers rich in  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ ; and mixtures of a clinker rich in  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  and ordinary Portland cement clinker. 15
5. A composition according to claim 1, 2 or 3, characterised in that the mineral clinker contains at least 25% by weight of  $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$ , not more than 1% by weight of free lime, less than 5% by weight of  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ , and not more than 10% by weight of  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ , said composition also comprising sufficient calcium oxide and/or calcium hydroxide to render the said clinker hydraulic. 20
6. A composition according to any one of claims 1 to 5, characterised in that it contains not more than 20% of calcium oxide and/or calcium hydroxide, relative to the total composition on a dry weight basis.
- 25 7. A composition according to any one of claims 1 to 6, characterised in that the air-entraining agent is selected from animal or vegetable fats or oils; natural wood resins and the alkali metal salts thereof; sulfated or sulfonated organic compounds; and amphoteric surfactants. 25
8. A composition according to any one of claims 1 to 7, characterised in that the stabilising agent is selected from gelatine, starches and cellulose ethers.
- 30 9. A composition according to any one of claims 1 to 6, characterised in that the air-entraining agent is an anionic surfactant selected from sulfated or sulfonated organic compounds and the stabilising agent is selected from cellulose ethers. 30
10. A composition according to any one of claims 1 to 9, characterised in that it also contains one or more components selected from extenders, clays, setting retarders and setting accelerators.
- 35 11. A method of forming a foamed cement, characterised in that a composition according to any one of claims 1 to 10 is mixed with water and a gas is introduced into the aqueous mixture to form a foam. 35
12. A method according to claim 11, characterised in that the amount of water is from 80 to 350% by weight of the mineral clinker (a).
13. A method according to claim 11 or 12, characterised in that the amount of gas introduced is from 40 86 to 95% of the resultant foamed cement on a volume basis. 40